# AN INFRARED STUDY OF CERTAIN WATER FREQUENCIES

BY

RICHARD SCHLEGEL, JR.

A.B., University of Chicago, 1935

M.A., State University of Iowa, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1943

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## ACKNOWLEDGMENT

This thesis was prepared under the direction of Professor W. H. Rodebush, and his counsel and guidance are gratefully acknowledged. Professor A. M. Buswell gave many valuable suggestions, and I wish to thank him for his interest and kindness in aiding the work. I am especially indebted to Dr. R. C. Gore. He was at all times in close touch with the work, both experimental and interpretive, and I sincerely appreciate the advice and assistance which he gave. Part of the work was done under a fellowship granted from the Rockefeller Foundation. I also wish to express appreciation to Professor R. G. Gustavson, of the University of Colorado, for his encouragement of my scientific education.

# AN INFRARED STUDY OF CERTAIN WATER FREQUENCIES

## Introduction

It can be shown by the methods of physical dynamics that the three atoms of the water molecule should possess three fundamental or normal modes of vibration. These are referred to as the $v_1$, $v_2$, and $v_3$ vibration frequencies. On the basis of molecular constants calculated from the observed water vapor spectrum, these frequencies can be assigned definite values. The most recent assignment, made by H. H. Nielsen[1], gives the values: $v_1 = 1595.4$ cm.$^{-1}$, $v_2 = 3652.7$ cm.$^{-1}$, $v_3 = /3756.8$ cm.$^{-1}$. The $v_1$ and $v_3$ frequencies have long been observed in the infrared spectrum of water vapor. The $v_2$ frequency seems to be masked by the much stronger absorption band of the $v_3$ frequency, although certain lines of the spectrum have been interpreted as arising from the $v_2$ frequency. Infrared activity for a given vibration is proportional to the total electrical dipole change involved in the molecular vibration. Geometric analysis shows that in the water vapor molecule the $v_3$ vibration would involve much greater dipole change than the $v_2$ vibration.

In the spectrum of liquid water a strong absorption band is observed at about 2.90 mu (3450 cm.$^{-1}$), and a band is observed at about 6.08 mu (1646 cm.$^{-1}$). These bands arise from the $v_3$ and $v_1$ vibration frequencies respectively. The displacement to longer wave lengths, compared with the vapor spectrum, is due to the molecular association in the liquid state. The $v_2$ frequency has not hitherto been reported as having been observed in the spectrum of liquid water. But infrared studies of solutions of water in the inert solvent, $CCl_4$, have given an indication of absorption resulting from the $v_2$ vibration[2]. The spectrum of water vapor, water, and ice has been generally studied and discussed by J. J. Fox and A. E. Martin[3].

## Results and Discussion

An apparatus to be used in conjunction with an infrared spectrometer was constructed for the purpose of making studies of thin solid or liquid films at various temperatures. In the apparatus, thermal control is achieved by means of a flowing stream of air.

The large 3 mu absorption band of liquid water was observed at temperatures ranging from 0° C. to 90° C. It was found that there is a shift of the absorption peak from 2.97 mu, at 0° C., to 2.90 mu at 90° C. Studies of dilute solutions of water in $CCl_4$ show that unassociated or monomeric water has an absorption maximum at 2.70 mu. The shift which we observed indicates a roughly linear shift with temperature rise, assuming that water would be unassociated at its critical temperature, 374° C., and would at that point have its maximum absorption at 2.70 mu. We observed no evidence of unassociated water in our studies. Apparently, then, all the molecules of liquid water are associated at ordinary temperatures. This association presumably involves hydrogen bonding between the molecules; and it is this bonding which causes the shift of the vibration frequencies as water passes from the vapor to liquid state. The observed shift to shorter wave-lengths seems to indicate that the strength of the hydrogen bond between water molecules decreases with temperature rise, since the vibration frequencies move toward the frequencies of an unperturbed, isolated water molecule.

Besides the major absorption peak in the 3 mu region, we observed in all of our studies of liquid water a secondary peak or hump, at about 3.07 mu (3257 $cm.^{-1}$). We suggest that this absorption arises from the $v_2$ vibration frequency of the associated liquid water molecule.

Studies were made of the spectrum of ice in the 3 mu region, at temperatures down to —15° C. The maximum absorption of ice was found to be at 3.07 mu, with a secondary hump at about 2.97 mu. The intensity of the 3.07 mu absorption in ice was much greater than that of the 2.93 mu absorption in water. The flowering of the 3.07 mu absorption in ice can be explained if we assume that the angle between the two O-H bonds in the water

molecule is smaller in ice than in water; for the motions of the hydrogen atoms in the $v_2$ vibration are such that the dipole change associated with the vibration is proportional to the cosine of one-half the bond angle. The amount of dipole change associated with the $v_3$ frequency, on the other hand, should decrease when the bond angle becomes smaller. It has previously been suggested by W. H. Rodebush[4], on other grounds, that the bond angle in the water molecule is greater in water than in ice.

An alternative interpretation of the ice and water spectra can be given on the assumption that the hydrogen bonding between the molecules is stronger in ice than in water. As a result, the perturbation of the $v_3$ frequency would be greater in ice, and a shift of the absorption peak to 3.07 mu could be thus explained. On this view, the 3.07 mu secondary peak in the water spectrum would be due not to the $v_2$ frequency, but to the presence of a certain amount of ice structure in liquid water. And similarly, the absorption at 2.97 mu in the ice spectrum would result from some water configuration present in the ice. It is probable that there is a small amount of ice structure in water, and of water structure in ice. The fact that we found the secondary 3.07 mu absorption band even in the spectrum of water at 90° C. is perhaps an argument against interpreting this absorption as arising from ice structure. Also, the increased intensity of the absorption of ice, as compared with that of water, is not readily explained by this alternative interpretation.

The alcohols show a strong infrared absorption at about 3 mu, arising from the vibrations of the hydrogen atom along the O-H valence bond. Thin films of methyl, ethyl, and butyl alcohols were studied at 23° C. and at —20° C. In each case it was found that at the lower temperature there was increased absorption at a longer wave-length, although intensity of absorption was about the same at the two temperatures. An equi-molecular mixture of ethyl alcohol and water was studied, at 23° C. and —20° C. In this case, the intensity of absorption was much smaller at the lower temperature. This result leads to the indication that in a water-alcohol solution the amount of water-alcohol molecular association decreases with temperature decrease.

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## VITA

The author was born in Davenport, Iowa, on August 29, 1913. He attended the Davenport schools, and was graduated from the Davenport High School in 1931. In September of that year he entered the University of Chicago, from which he received the A.B. degree in 1935. H was a scholar at the State University of Iowa the following year, and in June, 1936, received an M.A. degree at Iowa. For the year 1937-38 he held a university fellowship at the University of Chicago. Previous to this year his college work had been chiefly in philosophy, but during this year he changed the direction of his work to the physical sciences. From 1938 to 1940 he worked as a lecturer and demonstrator at the Museum of Science and Industry in Chicago. During the academic year 1940-41 the author was an assistant in chemistry at the University of Colorado. He entered the University of Illinois in September, 1941, and was a Special Research Assistant in the year 1941-42. For the year 1942-43 he is serving as an Assistant in Chemistry. The author is a member of Gamma Alpha and Sigma Xi fraternities. He has recently published "A View of Time", in Popular Astronomy, **51**, 83 (1943).

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